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CHEMISORPTION OF NITROGEN ON A PROMOTED IRON CATALYST

By

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Introduction

This paper, in conjunction with the foregoing one, will give the detailed characteristics of the chemisorption of nitrogen on an exhaustively reduced iron catalyst used for ammonia synthesis. A great deal of evidence exists to show that rates and equilibria for the chemisorption of gases on metallic catalysts can be modified by impurities such as oxygen remaining on the surface. Special precautions were therefore taken to reduce the iron catalyst as throughly as possible, and to keep mercury or grease vapor away from the catalyst during the course of the experiment.

The chemisorption measurements were made at temperatures from 300° to 500°C and at pressures ranging from 10^{-3} to 32 mm. mercury. Thermodynamic quantities of chemisorbed nitrogen molecules were derived as a function of the fraction of surface covered. It was thus found that a simple relation holds among thermodynamic quantities investigated.

Experimental

A 10.4 g. unreduced sample of ammonia synthetic iron catalyst containing 1.06% K_2O, 1.82% of Al_2O_3, 0.41% of SiO_2 and traces of MgO and CaO, supplied by *Toa Synthesis Co.* was placed in a U-type Pyrex bulb, and heated in a circulating stream of hydrogen at a pressure of about 600 mm. mercury to 550°C by means of an electric furnace. The water formed was condensed out by the liquid air traps attached close to either side of the U-type sample bulb. These traps were occasionally evacuated and fresh hydrogen then supplied.

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1) T. KWAN, J. Res. Inst. Catalysis, 3, 16 (1953).

The reduction of the catalyst was continued over a period of one month until hydrogen consumption became imperceptible within the experimental accuracy of the pressure measurement ± 1 mm. mercury. The water formation was estimated to be less than 0.1 mg. per hour at the end of the reduction. The catalyst was always outgassed at 550°C for three hours before being brought into contact nitrogen, and was reduced at 550°C over night between runs. The surface of the catalyst was found to be 135 sq. meters per total amounts of the sample by the B. E. T. method using nitrogen as adsorbate at the b. p. of liquid nitrogen.

The hydrogen initially used for the reduction was prepared by electrolysis but finally prepared by passage through a heated palladium thimble. Nitrogen was prepared by igniting sodium azide in a high vacuum. The temperature measurement of the catalyst was made with an alumel-chromel thermocouple placed in the center of the sample bulb and connected with a potentiometric regulator. The constancy of the temperature was ± 1°C. The pressure of nitrogen in the catalyst bulb was measured by the means of a McLeod gage and cathetometer. The dead space of the chemisorption system was measured by nitrogen under the same condition as the chemisorption measurement but in the absence of the catalyst. The technique employed in determining chemisorbed quantity has been described elsewhere.[2)]

Chemisorption Isotherm

A known quantity of nitrogen was admitted to the outgassed catalyst kept at a desired temperature. Above 450°C, the decrease in the pressure of nitrogen due to chemisorption became imperceptible within two or three hours after admission, but at 400°C or below it took more than twenty hours to reach a similar state. Therefore, above 450°C the pressure of nitrogen was always taken as being at equilibrium after the system stood overnight. At 400°C the system was allowed to stand more than two days. The next portion of nitrogen was then admitted and equilibrium pressures were determined in a similar manner.

Chemisorption isotherms were determined primarily at 450° and 500°C and a few points at 400°C. Several runs made by reducing the

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[2)] T. KWAN: J. Res. Inst. Catalysis, **1**, 81 (1949).

catalyst between runs have proved the reproducibility of the isotherms. These are shown in Fig. 1 which is a plot of the logarithm of chemisorbed quantity (in moles) *vs.* the logarithm of equilibrium pressure (in mm. mercury).

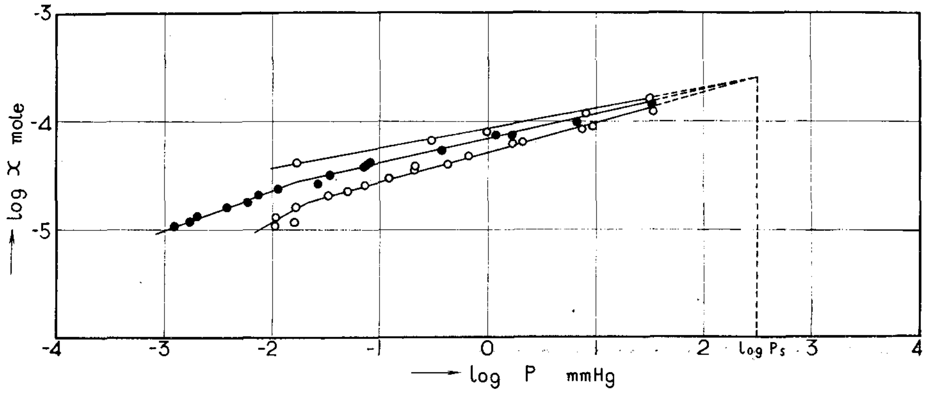

Figure 1. Chemisorption Isotherm of Nitrogen on a Promoted Iron Catalyst. T: 400°, 450° and 500°C. Ordinates represent chemisorbed quantities per total catalyst sample (10.4 g. unreduced material).

As shown in Fig. 1, the shapes of the isotherms resemble those for the hydrogen-tungsten system obtained by FRANKENBURG[3] and of the ammonia-ferric oxide system obtained more recently by CREMER.[4] Namely, the log-log plot of the isotherm, in the region of high equilibrium pressures, gave a fan-like convergency, if extrapolated linearly, and deviations from the straight line plot were found in the region of small equilibrium pressures.

The chemisorbed quantity at the common intersection was found to be 2.5×10^{-4} mole and the corresponding equilibrium pressure 320 mm. mercury. If we assume that the fraction of surface covered by nitrogen at the point of intersection corresponds to $\theta = 1$, the deviation from the log-log straight line of the isotherm occurs near $\theta = 0.08$.

The chemisorption isotherm, except for the coverage lower than 0.08, is now expressed as

$$\ln \theta = \frac{1}{n} \ln \frac{p}{p_s} \qquad (1)$$

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[3] W. G. FRANKENBURG, J. Am. Chem. Soc., **66**, 1827 (1944).

[4] E. CREMER, Z. Elektrochem., **56**, 439 (1952).

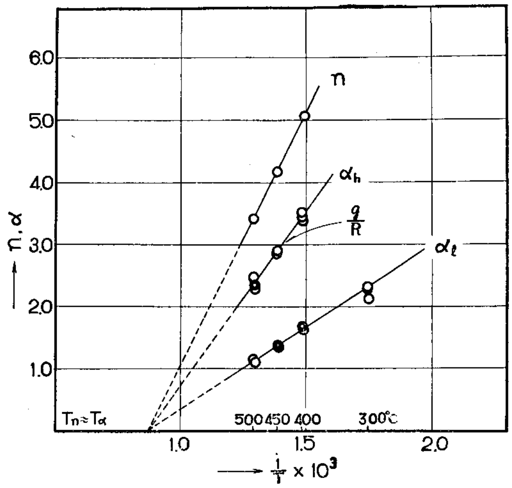

Figure 2. Temperature Dependency of n and α.

where p_s is the equilibrium pressure at the intersection and $\frac{1}{n}$ the slope of the log-log straight line. As shown in Fig. 2, n was found to be linearly dependent on the reciprocal of the absolute temperature. Let the slope of this straight line be $\frac{\gamma}{R}$, where R is the gas constant. Then n can be written in the form

$$n = \frac{\gamma}{RT} - \frac{\gamma}{RT_n} \qquad (2)$$

where $\frac{1}{T_n}$ is the intercept of the extrapolated straight line on the $\frac{1}{T}$ abscissa.

Evaluating γ from Fig. 2 as 16.5 kcal, we get from (1) and (2) the expression

$$q = -\gamma \ln \theta = -38 \log \theta \quad \text{kcal/mole} \qquad (3)$$

for the isosteric heat of chemisorption defined as $q = RT^2 \left(\frac{\partial \ln p}{\partial T}\right)_\theta$. Eq. (3) actually covers the range θ from 0.08 to 0.64. For the lower coverage, q was found to decrease monotonously from about 50 kcal/mole at the lowest coverage observed, $\theta = 0.04$, to 42 kcal/mole around $\theta = 0.08$.

Kinetics of Chemisorption

The decreasing pressure of nitrogen on the catalyst was determined after admission of the gas to the catalyst. Typical runs obtained at temperatures of 300°, 400° and 500°C are shown in Table 1 where p_0 is the pressure of nitrogen at time zero.

As mentioned elsewhere,[1] the process of chemisorption may in general be described by the expression[*]

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[*] This equation was derived assuming that the stoichiometric number due to HORIUTI (J. Res. Inst. Catalysis, **1**, 8 (1948)).

TABLE 1.

	Time min.	Pressure mm. Hg.	Time min.	Pressure mm. Hg.
$T = 300^\circ$C	0	1.74 (p_0)	21	1.15
	1	1.47	25	1.12
	2	1.425	27	1.105
	3	1.39	30	1.08
	5	1.34	35	1.06
	7	1.30	40	1.025
	9	1.28	45	1.00
	11	1.275	50	0.965
	13	1.255	60	0.95
	15	1.22		
	18	1.19		
$T = 400^\circ$C	0	1.728 (p_0)	16	0.815
	1	1.42	19	0.775
	2	1.285	22	0.74
	3	1.20	26	0.70
	4	1.15	30	0.66
	5	1.11	35	0.63
	6	1.07	40	0.60
	7	1.035	46	0.56
	10	0.94	52	0.53
	12	0.89	60	0.50
	14	0.855	70	0.465
			80	0.43
			90	0.415
$T = 500^\circ$C	0	1.399 (p_0)	12	0.375
	1	0.89	14	0.35
	2	0.735	16	0.33
	3	0.65	18	0.32
	4	0.58	21	0.30
	5	0.535	25	0.285
	6	0.50	30	0.265
	7	0.47	35	0.25
	8	0.45	40	0.235
	10	0.405		

$$-\frac{dp}{dt} = \vec{v}\left(1 - \frac{p_e}{p}\right) \qquad (4)$$

where $\vec{v}$ is the forward rate and p_e is the pressure of gas which would be in equilibrium with the chemisorbed quantity at time t, and can be estimated from the data of isotherm.

Below 400°C, p_e was very small compared with any p during the first few hours so that $1 \gg \frac{p_e}{p}$ can hold. Above this temperature, however, this relation did not always hold as shown in Table 2 for the run obtained at 500°C. In Table 2, the value of log $\left(-\frac{1}{p}\frac{dp}{dt}\right)$ or, as the case may be, $\log\left(-\frac{1}{p}\frac{dp}{dt}\Big/1-\frac{p_e}{p}\right)$ was determined at suitable times for each run.

TABLE 2.

T=300°C. p_0=1.74 mm. Hg.

T min.	P mm. Hg.	$-dp/dt$ mm. Hg. min.$^{-1}\times 10^2$	$\log\left(-\frac{1}{p}\frac{dp}{dt}\right)$	$\log(p_0-p)$
2.3	1.413	3.89	− 1.560	− 0.490
4.5	1.354	2.14	− 1.798	− 0.400
7.0	1.302	1.39	− 1.950	− 0.358
8.0	1.290	1.35	− 1.972	− 0.346
8.2	1.284	1.35	− 1.972	− 0.341
16.0	1.200	0.964	− 2.075	− 0.268
30.0	1.082	0.674	− 2.206	− 0.182
35.0	1.060	0.592	− 2.253	− 0.167
45.4	1.003	0.433	− 2.365	− 0.133

T=400°C p_0=1.728 mm. Hg.

1	1.42	18.3	− 0.890	− 0.511
2	1.285	10.0	− 1.109	− 0.353
3	1.205	7.07	− 1.231	− 0.280
4	1.15	5.31	− 1.336	− 0.237
6	1.07	3.75	− 1.455	− 0.181
8	1.00	3.25	− 1.488	− 0.138
10	0.94	2.81	− 1.524	− 0.103
20	0.765	1.14	− 1.826	− 0.016
25	0.71	0.90	− 1.879	0.008
30	0.667	0.777	− 1.933	0.026
40	0.60	0.583	− 2.037	0.053
50	0.545	0.50	− 2.101	0.073
60	0.50	0.392	− 2.106	0.090

$T = 500°C.$ $p = 1.399$ mm. Hg.

T min.	P mm. Hg.	$-dp/dt$ mm. min.$^{-1}\times 10^2$	$\log(p_0-p)$	p mm. Hg$\times 10^2$	$\log\left(-\frac{1}{p}\frac{dp}{dt}\Big/1-\frac{p_e}{p}\right)$
1.0	0.89	21.0	− 0.292	1.00	− 0.663
1.65	0.788	13.1	− 0.214	1.32	− 0.77
2.0	0.735	11.2	− 0.178	1.58	− 0.809
2.6	0.68	9.45	− 0.143	1.74	− 0.840
3.0	0.65	7.64	− 0.125	1.86	− 0.914
3.9	0.585	5.54	− 0.089	2.19	− 1.007
4.0	0.58	5.18	− 0.087	2.29	− 1.032
5.0	0.535	3.76	− 0.064	2.88	− 1.117
5.3	0.522	3.61	− 0.057	2.89	− 1.146
6.0	0.50	3.11	− 0.046	3.17	− 1.178
6.3	0.488	2.94	− 0.040	3.19	− 1.190
8.0	0.45	2.33	− 0.025	3.72	− 1.240
10.0	0.405	1.71	− 0.002	4.47	− 1.324
15.0	0.314	1.08	0.025	5.90	− 1.414

In Fig. 3, $\log\left(-\frac{1}{p}\frac{dp}{dt}\right)$ or $\log\left(-\frac{1}{p}\frac{dp}{dt}\Big/1-\frac{p_e}{p}\right)$ was plotted against $\log(p_0-p)$ together with the corresponding data obtained at 450°C.

As shown in Fig. 3, the log-log plot gave two linear portions with different slopes. Since the quantity (p_0-p) is proportional to the chemisorbed amount, the rate of chemisorption $\vec{v}$ may now be written in the form

$$\vec{v} = k_a p^{-a}\theta \tag{5}$$

where a and k_a are constants characteristic of a certain range of coverage. The apparently discontinuous change in the value of the slope or of a was found to occur around $\log(p_0-p) = -0.18$ corresponding to

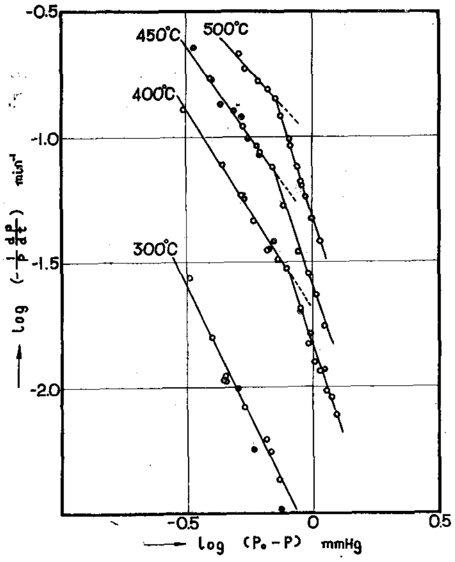

Figure 3. Chemisorption Rate of Nitrogen on a Promoted Iron Catalyst as a Function of Chemisorbed Quantity. T: 300°, 400°, 450° and 500°C.
For the run at 500°C, ordinates represent $\log\left(-\frac{1}{p}\frac{dp}{dt}\Big/1-\frac{p_e}{p}\right)$.

$\theta=0.074$. Several runs were made further to confirm the temperature dependency of α, and indicated that the discontinuity in the slope appears always around $\theta=0.08$. The temperature dependency of α is shown in Fig. 2 where α_h and α_l denote the slope above and below $\theta=0.08$ respectively.

As shown in Fig. 2, α was found to be a linear function of $1/T$. So it may be expressed as

$$\alpha = \frac{g}{RT} - \frac{g}{RT_\alpha} \qquad (6)$$

where g/R is the slope of the straight line and $1/T_\alpha$ the intercept on the $1/T$ axis.

From eqs. (5) and (6) the Arrhenius activation energy for the chemisorption becomes

$$E = RT^2\left(\frac{\partial \ln k}{\partial T}\right)_\theta = g \ln \theta + E_s \qquad (7)$$

where $k = -\frac{1}{p}\frac{dp}{dt}$, and E_s refers the quantity $RT^2\left(\frac{d \ln k_a}{dT}\right)$. The estimated value for g was 10.7 and 5.0 kcal respectively for the coverage higher and lower than 0.08. So the following expressions are given for the activation energy of the chemisorption of nitrogen:

$$\theta > 0.08 \quad E = 25 \log \theta + 38 \text{ kcal/mole} \qquad (8)$$

$$\theta < 0.08 \quad E = 11 \log \theta + 23 \text{ kcal/mole} \qquad (9)$$

In spite of the fairly good reproducibility attained in measuring both kinetics and equilibria for the chemisorption, the catalyst in a later period of the work has suffered to chemisorb nitrogen efficiently to a certain extent. The chemisorption rate of nitrogen was then determined with this "efficient" catalyst at a temperature of 400°C. Particular interest was given to the relation between $\log\left(-\frac{1}{p}\frac{dp}{dt}\right)$ and $\log(p_0-p)$. The results indicated that the plot consisted of three linear portions with the slopes of 0, 1.3 and 3.0 respectively varying with increased chemisorption. One discontinuity in the slope occurred at $\theta=0.025$. Another was found to occur around $\theta=0.08$ similar to that obtained for the "inefficient" state of the catalyst. These particular plots have been illustrated in the foregoing paper.[1)]

The rate of chemisorption was further determined at temperatures of 300°, 350° and 450°C with the efficient catalyst in the region of θ smaller than 0.025. The results indicated that the slope in the log-log plot, α, was always zero. The temperature coefficient of the rate constant equal to $\left(-\frac{1}{p}\frac{dp}{dt}\right)$ was estimated to be 8 kcal/mole in this sparsely covered surface.

The temperature coefficient of the chemisorption rate was not determined with this efficient catalyst for the high coverage because of the accidental breaking of the catalyst bulb. The re-reduction of the catalyst brought the catalyst to the former "inefficient" state but not to the "efficient".

Thermodynamic Properties of Chemisorbed Nitrogen Molecules

The above results enable us to evaluate thermodynamic quantities of chemisorbed nitrogen molecules such as ΔS and ΔS^* etc. Substituting for n in eqs. (1) and (2) yields

$$\frac{\gamma \ln \theta}{RT} = \frac{\gamma \ln \theta}{RT_n} + \ln \frac{p}{p_s} \tag{10}$$

From (10) and (3) we have

$$-q = -q \frac{T}{T_n} + RT \ln \frac{p}{p_s} \tag{11}$$

Using the thermodynamic relation, $\Delta H = T\Delta S + \Delta F$, and remembering that $\Delta F = 0$ and $-q = \Delta H$, we get the expression

$$\Delta S = \Delta H \frac{1}{T_n} + R \ln \frac{p}{p_s} \tag{12}$$

for the entropy of chemisorption. Taking the standard state in the gas phase as 1 atm., and allowing the perfect gas law, eq. (12) becomes

$$\Delta S^0 = \frac{\gamma}{T_n} \ln \theta - R \ln p_s \tag{13}$$

From eqs. (3) and (13), the expression for ΔF^0 can readily be written as

$$\Delta F^0 = \gamma \left(1 - \frac{T}{T_n}\right) \ln \theta + RT \ln p_s \tag{14}$$

Now we shall turn to the kinetic data. From eqs. (5) and (6) we have

$$-\frac{1}{p} \frac{dp}{dt} = k = k_a \exp \left(\frac{g}{RT_a} - \frac{g}{RT}\right) \ln \theta \tag{15}$$

According to the absolute rate theory, k_a may be expressed as

$$k_a = \frac{kT}{h} e \exp\,(\Delta S_s^*/R) \exp\,(-E_s/RT) \tag{16}$$

where ΔS_s^* denotes the entropy of activation and kT/h the usual meaning. The expression for the entropy of activation ΔS^* now comes from (15), (16) and (7) as

$$\Delta S^* = \frac{g \ln \theta}{T_a} + \Delta S_s^* \tag{17}$$

The thermodynamic relation, $\Delta F^* = E - T\Delta S^*$, yields the expression

$$\Delta F^* = g\left(1 - \frac{T}{T_a}\right) \ln \theta + \Delta F_s^* \tag{18}$$

for the free energy of activation. Here, ΔF_s^* is equal to $E_s - T\Delta S_s^*$.

As shown in Fig. 2, T_n was found to coincide with T_a. Due to this, a definite relationship exists among thermodynamic quantities investigated above. Proceeding from θ to $\theta + \delta\theta$ at a constant temperature, we have

$$\frac{\delta \Delta F^*}{\delta \Delta F^0} = \frac{\delta \Delta S^*}{\delta \Delta S^0} = -\frac{\delta E}{\delta q} = \frac{g}{\delta} \tag{19}$$

The value of g/γ was found to be 0.65 in the region of higher coverage.

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